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(54) Title of invention	Resin composition for hairdressing
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## Specification

### 1. Title of the invention

Resin composition for hairdressing

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### 2. Scope of the patent claims

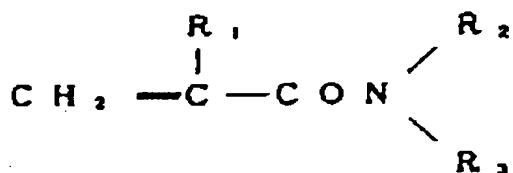
(1) A resin composition for hairdressing, obtained by copolymerizing polymerizable monomers a to e below then neutralizing using a water-soluble organic basic substance

10 a. from 6 to 35% by weight of at least one monomer chosen from the group consisting of acrylic acid, methacrylic acid and itaconic acid

b. from 15 to 50% by weight of at least one monomer from the C10-18 aliphatic alcohol esters of acrylic acid and/or methacrylic acid

15 c. from 15 to 50% by weight of at least one monomer from the C4-8 aliphatic alcohol esters of acrylic acid and/or methacrylic acid

d. from 5 to 50% by weight of at least one monomer chosen from N-alkyl-substituted acrylamides represented by the formula below



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(in the formula, R<sub>1</sub> and R<sub>2</sub> are H or CH<sub>3</sub>, and R<sub>3</sub> is an alkyl group from CH<sub>3</sub> to C<sub>8</sub>H<sub>17</sub> or C(CH<sub>3</sub>)CH<sub>2</sub>COCH<sub>3</sub>)

e. from 0 to 25% by weight of other vinyl-based monomer.

25 (2) The resin composition for hairdressing as claimed in claim 1, where the total amount of monomer b and monomer c is not less than 41% by weight.

(3) The resin composition for hairdressing as claimed in claim 1, where monomer d is diacetone acrylamide.

### 3. Detailed description of the invention

#### 30 Field of industrial use

The present invention relates to a resin composition for hairdressing having, in particular, excellent solubility with respect to liquefied petroleum gas (LPG) and which results in excellent hairdressing performance when setting hair in high temperature, high humidity environments.

#### 35 Prior art

Conventionally, nonionic resins and anionic resins are known as resins for hairdressing.

Known examples of abovementioned nonionic resins include polyvinylpyrrolidone, vinylpyrrolidone/vinyl acetate copolymers and polyvinyl methyl ether. However, polyvinylpyrrolidone-based substances are disadvantageous in that there is a considerable difference in physical properties before and after moisture absorption, that is, although films formed thereof are hard prior to moisture absorption, they quickly soften when they do absorb moisture, and moreover, flaking is exhibited during drying, and curls and sets are soon lost in humid conditions. Substances obtained by polymerizing vinyl acetate with vinylpyrrolidone do not result in a decrease in flaking, and the film formed has poor transparency and so the hair does not look natural. Moreover, polyvinyl methyl ether is merely added as plasticizer for polyvinylpyrrolidone, as it is very sticky.

The abovementioned anionic resins include vinyl ether/maleic anhydride half ester, vinyl acetate/crotonic acid copolymer and (meth)acrylic acid/(meth)acrylate ester copolymer, and substances such that the resin film has been rendered water-soluble by neutralization of the carboxyl groups in the polymer are currently in mainstream use in resins for hairdressing. However, the abovementioned anionic resins are disadvantageous in that many of them have poor solubility with respect to liquefied petroleum gas and insolubles can form during aerosol spraying at low temperature with formulations in which only liquefied petroleum gas is used, which can cause poor aerosol spraying or clogging, and its intended function cannot be achieved.

It should be noted that in the present specification, (meth)acrylic acid is used as a general term for acrylic acid and methacrylic acid, (meth)acrylate ester used as a general term for acrylate ester and methacrylate ester, (meth)acrylate used as a general term for acrylate and methacrylate, and (meth)acrylamide used as a general term for acrylamide and methacrylamide.

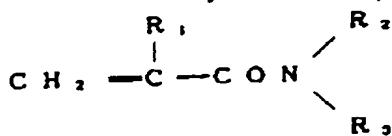
#### Problem to be overcome by the invention

The problem to be overcome by the present invention is the provision of a resin composition for hairdressing which gives excellent hairdressing performance even in high temperature, high humidity environments but does not result in the formation of insolubles when aerosol spraying is performed with formulations in which only liquefied petroleum gas is used, even at low temperatures.

#### Means of overcoming the problem, and use thereof

The inventive resin composition for hairdressing is obtained by copolymerizing polymerizable monomers a to e below then neutralizing using a water-soluble organic basic substance

- a. from 6 to 35% by weight of at least one monomer chosen from the group consisting of acrylic acid, methacrylic acid and itaconic acid
- 5 b. from 15 to 50% by weight of at least one monomer from the C10-18 aliphatic alcohol esters of acrylic acid and/or methacrylic acid
- c. from 15 to 50% by weight of at least one monomer from the C4-8 aliphatic alcohol esters of acrylic acid and/or methacrylic acid
- 10 d. from 5 to 50% by weight of at least one monomer chosen from N-alkyl-substituted acrylamides represented by the formula below



(in the formula, R<sub>1</sub> and R<sub>2</sub> are H or CH<sub>3</sub>, and R<sub>3</sub> is an alkyl group from CH<sub>3</sub> to C<sub>8</sub>H<sub>17</sub> or C(CH<sub>3</sub>)<sub>2</sub>COCH<sub>3</sub>)

- 15 e. from 0 to 25% by weight of other vinyl-based monomer.

The abovementioned monomer a contributes to the hair-washing properties and hydrophilicity of the resin, and is present at from 6 to 35% by weight, preferably from 10 to 30% by weight. If said amount used is less than 6% by weight, the resulting film becomes barely soluble in water and the hair-washing properties deteriorate, whereas if it exceeds 35% by weight, the amount of moisture absorbed increases and the stickiness becomes considerable, and solubility with respect to liquefied petroleum gas decreases.

Unsaturated carboxylic acid monomers chosen from the group consisting of acrylic acid, methacrylic acid and itaconic acid can be used individually or in combination as the monomer a.

Monomer b contributes to the lipophilicity, softness and hair-washing properties of the resin, and the amount used is from 15 to 50% by weight, preferably from 20 to 45% by weight. If said amount used is less than 15% by weight, the resulting film becomes hard, flaking occurs and the solubility with respect to liquefied petroleum gas deteriorates. If more than 50% by weight is used, however, the resulting film becomes very soft and exhibits stickiness, and the hair-washing properties deteriorate.

Specific examples of monomer b include synthetic alcohol (meth)acrylates such as decyl (meth)acrylate, lauryl (meth)acrylate, myristyl

(meth)acrylate, palmityl (meth)acrylate, stearyl (meth)acrylate, oleyl (meth)acrylate and tridecyl (meth)acrylate, and these may be used individually or in combination.

Monomer c also contributes to the lipophilicity, softness and hair-washing properties of the resin, and here too, the amount used is from 15 to 50% by weight, preferably from 20 to 45% by weight. If the amount used is less than 15% by weight, solubility with respect to liquefied petroleum gas decreases, whereas if it exceeds 50% by weight, the hair-washing properties deteriorate.

Specific examples of monomer c include n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, n-hexyl (meth)acrylate, n-octyl (meth)acrylate and 2-ethylhexyl (meth)acrylate, and these may be used individually or in combination.

Comparing the abovementioned monomer b and monomer c, monomer b makes a greater contribution than monomer c to the lipophilicity of the resin and results in greater deterioration of the hair-washing property, and monomer b also makes a greater contribution than monomer c to the solubility with respect to liquefied petroleum gas. The total amount of monomer b and monomer c is preferably no less than 41% by weight, in order to further improve the solubility with respect to liquefied petroleum gas.

Monomer d contributes to improving the set strength at high temperature and high humidity without adversely affecting solubility in liquefied petroleum gas, and contributes to film hardness. The amount used is from 5 to 50% by weight, preferably from 10 to 45% by weight. If less than 5% by weight is used, there is no improvement in setting [power] at high temperature and high humidity, whereas if more than 50% by weight is used, the film becomes hard and texture is adversely affected.

Specific examples of monomer d include diacetone (meth)acrylamide, N,N-dimethyl (meth)acrylamide, N-isopropyl (meth)acrylamide and N-octyl (meth)acrylamide, and these may be used individually or in combination. Excellent set strength can be maintained at high temperature and high humidity particularly when monomer d is diacetone acrylamide.

Monomer e contributes to the solubility in liquefied petroleum gas and film hardness. It is used if necessary, and the amount used is from 0 to 25% by weight. In order to achieve the desired results, it is preferable to use at least 1% by weight, although if the amount used exceeds 25% by weight, the solubility in liquefied petroleum gas decreases.

Specific examples of monomer e include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, ethoxyethyl (meth)acrylate, acrylonitrile, (meth)acrylamide, vinyl acetate, styrene and vinylpyrrolidone, and these may be

used individually or in combination. Of the abovementioned monomers e, the use of methyl acrylate, ethyl acrylate, propyl acrylate, ethoxy ethyl acrylate, acrylonitrile, acrylamide and vinylpyrrolidone results in a relatively soft film, whereas the use of methyl methacrylate, ethyl methacrylate, propyl methacrylate, ethoxy ethyl methacrylate, methacrylamide, vinyl acetate and styrene results in a harder, less sticky film.

Copolymerization of the abovementioned monomers a to e can be achieved by common solution polymerization in hydrophilic solvent, for example, it can be achieved by dissolving each monomer in the hydrophilic solvent, adding polymerization initiator then agitating at a temperature equal or close to the boiling point of the solvent, under a current of nitrogen. The abovementioned monomers can be copolymerized either by having the total amount of all types present from the beginning of the polymerization, or by adding portions of the monomers, divided according to type and/or amount. The abovementioned solvent is preferably used such that there is from 30 to 60% by weight solid component in the resin solution.

Examples of hydrophilic solvents include aliphatic alcohols which dissolve in water, such as methyl alcohol, ethyl alcohol, isopropyl alcohol and butyl alcohol, and alcohols which contain water, such as 95% ethyl alcohol, and acetone, methyl cellosolve, ethyl cellosolve, dioxane, methyl acetate, ethyl acetate, dimethyl formamide and the like, and these can be used individually or in combination.

It is preferable to use, for example, a peroxide compound such as benzoyl peroxide or lauryl peroxide, or an azo-based compound such as azobisisobutyronitrile, as the polymerization initiator.

By adding water-soluble organic basic substance to the resin-containing solution obtained by the abovementioned copolymerization, it is possible to render the copolymerized resin water-soluble and neutralize it, preferably to a neutralization rate of from 50 to 100%,

Examples of water-soluble organic basic substances include ammonia, morpholine, (mono-, di- or tri-)ethanolamine, (mono-, di- or tri-)isopropanolamine, aminomethyl propanolamine, aminoethyl propanolamine, aminomethyl propanediol and aminoethyl propanediol, and these may be used individually or in combination. Specifically, when organic amines are used, the resulting working composition does not contain water and so these are suitable in the production of aerosols which repel water.

Resin compositions obtained as described above have a copolymer average molecular weight of from 5 000 to 200 000, and can be used either as the hydrophilic solvent solution obtained as a result of the abovementioned

copolymerization, without further modification, or as a water-containing solvent system.

The inventive resin compositions can be obtained as aerosols by dissolving said composition in hydrophilic solvent such as C1-4 aliphatic alcohol, water-containing alcohol such as 95% ethyl alcohol, acetone, methyl cellosolve, ethyl cellosolve, dioxane, methyl acetate or ethyl acetate, then pressure-loading the resulting solution into a container together with propellant. Examples of said propellants include liquefied petrochemical gas (LPG) having as main components propane, butane and isobutane; halogenated hydrocarbons having as components trichloromonofluoromethane (fluorocarbon 11), dichlorodifluoromethane (fluorocarbon 12), dichlorotetrafluoromethane (fluorocarbon 114), methylene dichloride and the like; and dimethyl ether, carbon dioxide and the like, and these can be used individually or mixtures thereof can be used. Aerosol can be obtained, for example, by dissolving the abovementioned resin composition in hydrophilic organic solvent so that the solids content in the resin composition is from 0.5 to 15% by weight, then loading from 25 to 80% by weight of solution thus obtained and from 75 to 20% by weight of abovementioned propellant into a pressurized vessel.

Inventive resin compositions can be dissolved in water and hydrophilic organic solvent, then various hairdressing reagent additives can be added so that the inventive resin composition can be used as a component for hairdressing reagents such as hair creams, hair lotions, non-gas aerosols (hair mists) and the like. The abovementioned resin composition can also be mixed with hair colorants, as a hair colorant fixer, and used in colorants for hair cosmetics such as color sprays, color foams, mascara-type cosmetics and the like. In addition to these uses, the abovementioned resin composition is also suitable for use as a film-forming component for face packs and a coating agent for skin wounds.

#### Working Examples 1 to 6

The present invention is described below based on working examples. It should be noted that "%" and "parts" disclosed below are both based on weight.

Table 1 shows the monomer compositions, degree of neutralization, average molecular weight and the like for the resins of the working examples and corresponding comparative examples, and table 2 shows the physical property appraisals for the resin composition shown in table 1.

#### Resin composition production

200 parts of polymerizable monomers a to e, 100 parts of ethyl alcohol and from 0.5 to 4 parts of polymerization initiator were introduced into a 1 l four-necked flask provided with a reflux condenser, thermometer, glass tube for nitrogen substitution, dropping funnel and agitator, and the system was polymerized for 5 h

under reflux (approximately 80°C) under a current of nitrogen. After polymerization, the system was cooled then an ethyl alcohol solution of water-soluble organic basic substance was added at 50°C and the system was diluted using ethyl alcohol to a solids content of 50%.

5      **Aerosol (hairspray) preparation**

Three types of aerosols (hairsprays) A to C having the compositions described below were prepared using the abovementioned resin compositions (solid content 50%) of the working examples and comparative examples, and A to C were loaded into pressure-resistant glass bottles for aerosol use.

	A	B	C
Ethyl alcohol solution (solids content (10%) of resin composition	45	50	55
Liquefied petroleum gas*	55	50	45

10     \*Liquefied petroleum gas comprising 25% propane and 75% butane, used at 20°C, approximately 3.0 kg/cm<sup>2</sup>

Appraisal of properties

(1) Aerosol stability

15     The hairsprays A, B and C that were obtained according to the abovementioned aerosol (hairspray) preparation were left for 24 h in a -10°C freezer, then the solutions were appraised as follows.

O: transparent

Δ: slightly cloudy

20     ×: separation or sedimentation

(2) Set strength (curl retention)

25     Approximately 2 g of hair length 22 cm was washed using a commercially available shampoo, treated using a commercially available rinse and then dried. Then a 10 g clip was attached to the ends of the hair, and attached to a motor which rotates 30 times per minute so that the hair does not fly away during spraying. Next, while the hair was rotating, hairspray was sprayed evenly for 10 s from a distance of approximately 15 cm, and the adhered droplets were immediately evened out by hand, and [the hair was] wound on a rod of a diameter of 1.2 cm, and this was secured using a clip then dried for 30 min at from 55 to 60°C. This was then  
30     cooled thoroughly in a desiccator then fastened as a spiral, then an upright glass plate (having gradations marked every 0.5 cm) was affixed perpendicularly, and this system was kept at from 38 to 40°C, 95% relative humidity in a humidity-controlled constant temperature/humidity vessel for 10 h, then the position of the tips of the

hair was recorded and the curl retention was determined according to the formula below.

$$\text{curl retention } (\%) = \frac{L - L_t}{L - L_0} \times 100$$

L: length of extended sample (L = 22 cm)

- 5 L<sub>0</sub>: position of the tip of the sample prior to being inserted into the constant temperature/humidity vessel  
Lt: position of the tip of the sample after 10 h in the constant temperature/humidity vessel

(3) Flaking power

- 10 Hair obtained in the same way as for the said strength appraisal was combed out and the amount of resin which fell during said combing was appraised as described below:

O: almost no resin fell

Δ: a small amount fell

- 15 x: a large amount fell

(4) Smoothness

Ease of combing during the flaking appraisal was appraised as shown below.

O: combing was easy

- 20 Δ: combing was slightly difficult

x: combing was difficult

(5) Film properties (washing properties and blocking)

- 25 Fixed amounts of solution prior to aerosol formation were spread over glass plates to approximately the same area (a diameter of approximately 1.5 cm) using a glass rod or the like. The glass plates were left overnight at 20°C, 60% relative humidity, then dried for 1 h at 60°C.

The abovementioned glass plates were immersed in 40°C aqueous solution containing 0.5% commercial shampoo, and the solubility of the films was appraised as shown below, to assess the washing properties.

- 30 O: dissolved within 1 h  
Δ: a small amount remained after 1 h  
x: much remained after 1 h.

The abovementioned glass plates were kept overnight in a constant temperature/humidity vessel at 30°C, 90% relative humidity, and the feel to the touch was appraised as follows, to assess blocking (stickiness).

- O: no stickiness
- Δ: slight stickiness
- x: considerable stickiness

(6) Feel

5           The feel was appraised as shown below by feeling by hand hair obtained as in the set strength appraisal.

- O: soft with good feel
- Δ: slight starchy or sticky feel
- x: considerable starchy or sticky feel.

Table 1 Monomer composition (parts), degree of neutralization (%) and average molecular weight ( $\times 1000$ ) of the resin

		Working example						Comparative example					
		1	2	3	4	5	6	1	2	3	4	5	6
Monomer a	acrylic acid		25	20	30		20		35	20	30		20
	methacrylic acid	20	25	20	20	30		10	35	20	20	30	
	itaconic acid		10			10			10			10	
Monomer b	lauryl acrylate	40						40					
	lauryl methacrylate		40	20			50		40	10			40
	myristyl methacrylate				90	40					110	40	
	stearyl acrylate		40	20					40	10			
Monomer c	butyl acrylate	40				40		50					40
	butyl methacrylate	40	40	30				40	20	50			
	ethylhexylacrylate				30		30				30		30
	ethylhexyl methacrylate			40		50				40		50	
Monomer d	diacetone acrylamide	60	20			20	90	60	20				110
	dimethylacrylamide			30						30			
	isopropylacrylamide				20						10		
Monomer e	methyl methacrylate				10	10						30	
	ethyl methacrylate			20						20			
Polymerization initiator	benzoyl peroxide	2	2	.				2	2				
	lauroyl peroxide				2	2					2	2	
	azobisisobutyronitrile				1		1			1		1	
Organic basic substance	monoethanolamine	11.3				12.3		12.8				12.3	
	triethanolamine			53.4						53.4			
	aminomethylpropanol				34.7						34.7		
	aminoethylpropanediol		51.9			24.0		58.6			24.0		
	morpholine					16.0						16.0	
Degree of neutralization of the resin (%)		80	55	70	60	80	80	90	55	70	60	80	80
Number average molecular weight of the resin ( $\times 1000$ )		85	110	80	100	90	75	80	110	85	95	90	80

Table 2 Appraisal of properties

		Working example						Comparative example					
		1	2	3	4	5	6	1	2	3	4	5	6
Aerosol stability	hairspray A	○	○	○	○	○	○	○	×	×	○	○	×
	hairspray B	○	○	○	○	○	○	○	×	×	○	○	×
	hairspray C	○	○	○	○	○	○	○	×	△	○	○	△
Curl retention (%)		74	72	70	70	72	75	63	58	60	56	53	74
Flaking		○	○	○	○	○	○	○	×	△	○	△	△
Smoothness		○	○	○	○	○	○	△	×	△	△	△	△
Film properties	stickiness	○	○	○	○	○	○	△	×	○	△	○	○
	washing properties	○	○	○	○	○	○	×	○	○	×	○	○
		○	○	○	○	○	○	△	×	△	×	△	△

Advantages of the invention

As described above, the inventive resin composition for hairdressing has excellent solubility, particularly with respect to liquefied petroleum gas, excellent smoothness with no stickiness or flaking, and excellent set strength even at high temperatures and in high humidity, and hairdressing performance can be achieved with no adverse effect on feel, and it can easily be removed on washing the hair.

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